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6 "Energies and Conformations of Molecules"

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Completed Project Summary

Abstract:

Energies and conformations of molecules were investigated in several different ways. The effect of angular distortion was studied by ab initio calculations of the energies of variously distorted methanes. The results could be related to the deformation energies found in small ring compounds. The photoelectron spectra of a series of cycloalkenes and methylenecycloalkanes were studied and the ionization potentials compared with the results of ab initio calculations. A remarkably good linear relationship was found, from which information on the reorganization energy and change in correlation energy on going to the ions could be derived.

Vibrational intensities in ethylene and related molecules were examined and led to information on the magnitudes of bond dipoles, and to charge distributions. Again, comparison with ab initio calculations provided the key to understanding the intensities.

The ultraviolet spectrum of bicyclobutane and of various deuterium substituted derivatives was examined. The high resolution spectrum of the first transition permitted us to determine the equilibrium geometry of this state.

An automated calorimetric system was developed. The heats of isomerization of quadricyclane, tricyclo[4.1.0.0^{2,7}]octane and benzvalene were determined.

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Results

1. Deformation Energies It is important to learn how and why energies of molecules change when distorted. This has been studied by calculating (ab initio) the change in energy of methane for several deformation modes.^{1, 3} The principal component of the energy change was nuclear repulsion. The results were used to estimate the distortion energies of a series of small ring compounds, and gave generally good results.

2. Photoelectron Spectra The principal experimental tool for obtaining molecular orbital energies is photoelectron spectroscopy. Both the HeI and HeII spectra for a series of cycloalkenes and methylenecycloalkanes were obtained.^{4, 7} The mo energy levels were calculated and compared with the ionization potentials. A good linear relationship was found. This permitted us to determine how the reorganization energy and the change in correlation energy on going to the ion change as a function of the mo energy.

3. Ultraviolet Spectra The medium resolution spectrum of bicyclobutane and of several of its deuterium labeled derivatives was obtained, and the high resolution spectrum of the first electronic transition also was obtained.^{11, 12} An analysis of the latter showed that the equilibrium excited state was planar and "kite" shaped. The infrared spectrum of bicyclobutane also was studied and a vibrational assignment and normal coordinate analysis was carried out. These data made it possible to analyze the ultraviolet spectrum.

4. Vibrational Intensities The reason for the difference in intensity

of the ir active bending modes in ethylene was studied using ab initio calculations. It was found that contrary to common belief, the out-of-plane mode involved no rehybridization.⁶ We were able to derive the C-H bond dipole and to explain the lower intensities of the other bending modes. Application of this model to other systems made it possible to obtain C-H bond dipoles for a variety of systems.⁹ The μ_{CH} values were linearly related to % s character of the nmr J_{13C-H} . Further development of this model should permit the routine calculation of charge distributions and of the intensities of the ir bands in any hydrocarbon.

5. Calorimetric Studies We have developed an automated calorimeter using a quartz thermometer as the sensing element and a minicomputer as the data collection device.² Calorimetric studies were made of the metal catalyzed isomerizations of quadricyclane,⁵ tricyclo[4.1.0.0^{2,7}]heptane (a bicyclobutane derivative)⁵ and benzvalene.⁸ These data are useful for obtaining heats of formation, and in the case of benzvalene, it gave important data concerning the mechanism of the thermal rearrangement to benzene.

Personnel

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20. Abstract

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